

Binding energies of $4d^6 5s^2$ states in Tc^-

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Relativistic configuration-interaction calculations predict the $\text{Tc}^- 4d^6 5s^2 J=4,3,2,1,0$ levels are bound to the neutral Tc I ground state by 636, 552, 503, 481, and 460 meV, respectively. The $J=4$ value is in good agreement with a revised semiempirical estimate presented here.

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I. INTRODUCTION

Electron affinities (EA's) for most of the bound neutral transition-metal atoms have now been measured [1]. Prior to some of these measurements, semiempirical EA's were available [2,3], which generally had good predictive value, when viewed as an s attachment to a $d^n s$ atomic state. The EA of Tc I remains the single unmeasured quantity that is unambiguously predicted to be bound [1–3] by 0.55(20) eV semiempirically. We revise this prediction to 0.658 eV in this work, as explained below.

Tc I is the middle element of the VIIA group, which consists of Mn I, Tc I, and Re I. A plot of s -electron binding energies (BE's) with respect to the lowest $d^n s$ level for each of the transition series vs n , the d shell occupancy, yields two nearly linear features [2]. The first has a negative slope through $n=3$ to $n=5$, where the d subshell approaches its half-full point. The other increases linearly through $n=0$ (no d electrons) and the range $n=7$ to $n=10$. The expectation is that the Mn^- , Tc^- , and Re^- s -electron BE's with respect to each corresponding $d^6 s$ threshold ($n=6$) follow the linear trend of the $n=7$ to $n=10$ data. Semiempirical values calculated from data available in the mid-80s [1–3] suggest s -electron binding energies of ~ 0.96 eV for both Mn^- and Tc^- and ~ 1.6 eV for Re^- . However, the ground states of Mn I, Tc I, and Re I are from the $d^{n-1} s^2$ configuration, so these BE's must be adjusted by the energy difference to the excited $d^n s$ states (2.11, 0.32, and 1.46 eV [4], respectively), resulting in semiempirical estimates [1–3] of <0 , 0.55(20) eV, and 0.15(15) eV, respectively. The resulting ordering of EA's of $\text{Tc} > \text{Re} > \text{Mn}$ is similar to the groups (Ti,Zr,Hf) and (V,Nb,Ta) where the EA's are also largest for the fourth row (second transition series) element.

In the interest of improving these semiempirical estimates, we have performed our own linear least-squares fit to the latest available experimental measurements [1,5–8] for the second transition series $n=7$ to $n=10$ (Ru^- to Ag^-), resulting in a predicted Tc^- EA of 658 meV with respect to the $4d^5 5s^2$ ground state. A similar fit to the third transition series data produces a revised estimate for the Re^- EA of 61 meV. As presented in Secs. II and III, our calculated $\text{Tc}^- J=4 4d^6 5s^2$ EA is 636 meV, in good agreement with this revised estimate. Similar relativistic configuration-interaction (RCI) calculations on Re^- are too near the ground-state threshold (<10 meV unbound) to give a conclusive prediction as to whether Re^- is bound or unbound.

First-principles RCI results have had good success in predicting EA's of transition-metal atoms such as Ru [6] and Os [9], in the former case simultaneous with experiment [6], and in the latter, preceding experiment. With time, our calculations have become more sophisticated in their more thorough treatment of second-order effects and shallow core contributions and in better optimization of the radial basis.

II. METHODOLOGY

Our RCI wave functions are built up from determinantal functions whose one-electron radial functions are taken from a Dirac-Fock (DF) calculation using the Desclaux's program [10]. Our basis members, or parents, are linear combinations of these determinants created by direct diagonalization of the J^2 matrix such that each basis member is an eigenfunction of J^2 , J_z , and the parity operator. The final RCI wave function is a linear combination of DF parents and correlation configuration parents calculated through diagonalization of the Hamiltonian matrix.

In general, our RCI bases consist of all single and double excitations out of the DF manifold that are important for the property of interest. In the case of an EA study, we need only include configurations that have differential energy contributions between the neutral and negative-ion states. Omission of corresponding configurations with nearly equal energy contributions in both states is important due to the fact that the DF manifold can become over correlated with respect to correlation configurations, leading to an artificial pulling away from the correlation manifolds [11,12]. Since the coefficient (and thus the energy contribution) of a given correlation configuration is inversely proportional to the energy difference between its manifold and the DF levels, this pulling away can cause nonnegligible losses in energy contributions of nearby energetically large configurations [11,12].

In the case of Tc^- we avoid a large amount of over correlation by treating the $\text{Tc}^- 4d^6 5s^2$ levels as s attachments to the excited $4d^6 5s J=9/2$ state in Tc I (319 meV [13] above the $4d^5 5s^2 J=5/2$ ground state). This allows us to omit $4d^2$ pair excitations that are nearly equal in both species due to the common occupation of the $4d$ subshell. For example, limited test calculations of the largest $4d^2$ pair excitation, $4d^2 \rightarrow f^2$, show a differential contribution between the neutral and negative-ion states of only ~ 5 meV, while the correlation contribution is over 1.7 eV in each state. Direct treatment of the $4d^6 5s^2$ Tc^- states as d attachments to the $4d^5 5s^2 J=5/2$ Tc I ground state (the true physical mecha-

nism) would require inclusion of these $4d^2$ pair excitations, adding ~ 2.5 eV of extra correlation that would likely introduce second-order losses in important correlation configurations far in excess of the 10–20 meV error introduced in their omission in the s attachment approach.

Even with the above reduction of the total correlation, we still note one problem configuration that exhibits marked losses between small few configuration calculations and the final RCI calculations. The double excitation $5s^2 \rightarrow p^2$ contributes ~ 500 meV to the $4d^6 5s^2$ energy in a small two configuration calculation, but loses over 130 meV as we near completion of our basis set. We attribute this loss partly due to difficulties in optimization of our “virtual” radials, denoted $v\ell$. These are our radial wave functions that represent orbitals not occupied in the DF manifold. They are relativistic screened hydrogenic functions with effective charges Z^* , which are optimized during an energy minimization procedure. For an initial vp orbital we find that optimization in the presence of all single and double valence excitations (excluding $4d^2$ pairs as discussed earlier) results in a Z^* of ~ 1.7 , whereas the Z^* that optimizes $5s^2 \rightarrow p^2$ in a small two configuration calculation is ~ 1.0 . The larger $Z^* = 1.7$ value for the initial vp optimizes the much larger (by ~ 200 meV) $4d5s \rightarrow pf$ excitation, and while inclusion of a second and third virtual p (vp' and vp'') serves to saturate the two configurations, neither contributes as much as it does in the smaller test calculations. Inclusion of two virtual p 's with $Z^* = 1.0$ and $Z^* = 1.7$ is insufficient as the vp' radial must be orthogonalized to the vp radial, and the resulting $Z^* = 1.7$ vp' is quite different from the single $Z^* = 1.7$ vp of a calculation with a single set of virtuals. We thus conclude that second-order effects are required to correct these losses (see Sec. III for more details).

The process of basis set saturation is further complicated by the observation that our core-valence pair excitations ($4p$ - $5s$ pairs) show contributions much lower than expected when comparing to results in our previous study of $\text{Ru}^- 4d^7 5s^2$ levels [14]. Normally we approach our basis construction by “layering” of virtual orbitals, with the first set optimized in the presence of valence excitations only, the second set optimized to valence and core-valence excitations, and the third or fourth sets of virtuals added as needed for further opening of the core subshells or saturation of core excitations. In the case of Tc^- we find the $4p$ - $5s$ pair excitations are also very sensitive to the Z^* of the initial set of virtuals (the one that has $\langle r \rangle$ most similar to the $5s$ DF radial). A choice of $Z^* = 1.5$ for the initial vp radial creates a change in total $4p$ - $5s$ pair excitations of ~ 80 meV. Again, inclusion of a vp'' orbital with $Z^* = 1.5$ is not a solution to the problem as it is necessarily orthogonalized to both vp and vp' , and greatly changed from a $Z^* = 1.5$ single vp in the process. With this in mind we deviate from our normal layering prescription of basis set creation and iterate both the first and second sets of virtuals in the presence of valence and core-valence excitations (the resulting initial vp does, in fact, have a $Z^* \sim 1.5$). A third set of virtual orbitals is then added to the larger configurations that do not appear saturated after inclusion of the first two sets.

TABLE I. Contributions to the RCI energies (in meV) of $\text{Tc}^- 4d^6 5s$ $J=9/2$ and $\text{Tc}^- 4d^6 5s^2$ $J=0$ states. Grouped contributions in the middle of the table exclude each of the four most important configurations listed separately in the first top four entries. “1O” indicates the $J=0$ calculation with first-order terms only. “2O” indicates $J=0$ calculations with second-order triple (T) and quadruple (Q) excitations.

Excitation	$J=0$		$J=0$ 2O	$J=0$ 2O
	$J=9/2$	$J=0$ 1O	(T)	($T+Q$)
$5s^2 \rightarrow p^2$ ^a	<i>N/A</i> ^b	−367	−417	−460
$4d5s \rightarrow p^2$	−95	−311	−333	−344
$4d5s \rightarrow sd$	−150	−257	−270	−275
$4d5s \rightarrow pf$	−521	−698	−706	−714
$5s \rightarrow \ell$	−14	−129	−143	−142
$4d \rightarrow \ell$	−166	−204	−207	−208
$5s^2 \rightarrow \ell^2$	<i>N/A</i> ^b	−104	−97	−96
$4d5s \rightarrow \ell^2 + \ell \ell'$	−57	−108	−109	−109
$4p^2 \rightarrow s^2 + sd$	−50	−25	−25	−25
$4p5s \rightarrow \ell \ell'$	−190	−319	−319	−317
Total RCI	−1242	−2522	−2626	−2687
DF				
(with respect to $J=9/2$)	0	666	666	666
$J=0$ BE		295	398	460

^aThe main “problem” configuration, $4d^6 vp^2$.

^bNot applicable.

One further simplification is made with regard to our basis set creation. We note that the differences in RCI energies between the different $4d^6 5s^2$ levels is very stable between stages in our calculations, changing less than 1 meV as the bases are built up. We use this fact to our advantage in the final calculations, where the relatively complicated second-order effects are added, by referencing each of the $J=1$ to $J=4$ levels to the much simpler $4d^6 5s^2$ $J=0$ state. By doing so we are able to include the second-order effects we require without relying on the computationally costly methods, such as our REDUCE [15,16] approximation, while remaining within our currently coded limit of 20 000 basis members (the final $J=0$ calculation has 10 324 parents, whereas the corresponding $J=4$ calculation would require nearly 35 000 parents). Thus our Tc^- BE's are calculated from the difference in the energies of the $4d^6 5s^2$ $J=0$ and $4d^6 5s$ $J=9/2$ levels, adjusted for the experimental energy difference of 319 meV [13] between the neutral threshold and the $4d^5 5s^2$ $J=5/2$ ground state and the stable energy differences between the $4d^6 5s^2$ levels as taken from intermediate stages of the Tc^- basis set creation.

III. RESULTS

Table I summarizes the energy contributions of the four most important individual correlation configurations, with the remaining excitations grouped by type. The first two columns give the first-order contributions to the $4d^6 5s$ $J=9/2$ threshold and the $4d^6 5s^2$ $J=0$ reference level, respectively. The third column is for a calculation including two types of

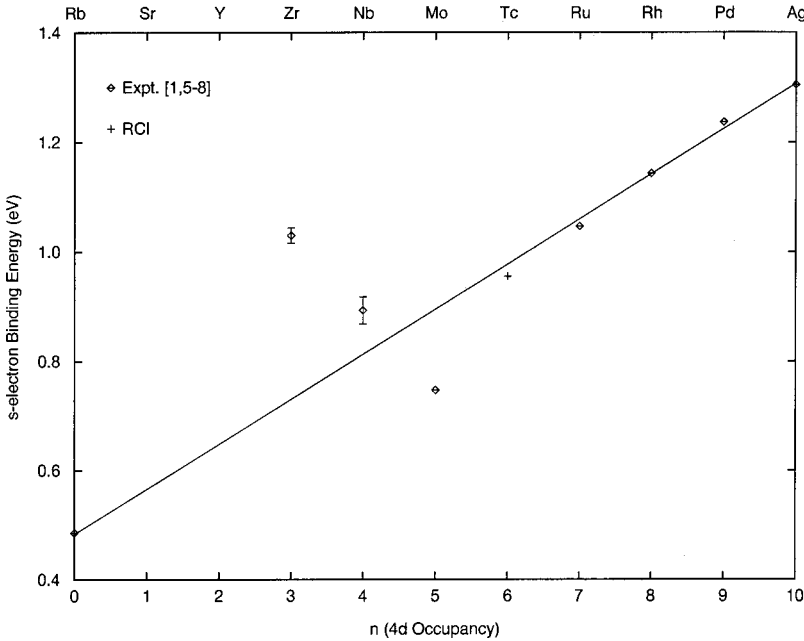


FIG. 1. Binding energy (eV) of $4d^n 5s^2$ negative-ion states [1,5–8] relative to the lowest $4d^n 5s$ neutral threshold.

second-order effects, relaxation of the $5s^2$ pair excitation j restrictions and $4d5s^2$ triple excitations. A separate (unpublished) calculation shows that removing the restriction of $j=0$ on the $v\ell^2$ subgroup of the $5s^2 \rightarrow v\ell^2$ excitations lowers the RCI energy by ~ 10 meV, primarily through increases in single $5s$ excitations, though a few meV of this increase is from $4d^6vp^2$, our “problem” configuration. Triple excitations are included to add correlation to $4d^6vp^2$ in the form of $4d-vp$ pair excitations to compensate for the over correlation of the $4d^65s^2$ DF manifold by the inclusion of the $4d-5s$ pair excitations. Accordingly, we include only those triples that contain at least one vp electron: $4d5s^2 \rightarrow sp^2 + p^2d + p^2g + spf + pdf + pfg$ (small test calculations show other possible triples, such as $4d5s^2 \rightarrow s^2d$ have a negligible effect on the RCI energy, ~ 1 meV or less). Note that both of these types of second-order effects contain the $5s^2$ subgroup, which is not present in the Tc $4d^65s$ threshold, so no complimentary effects need to be added in the neutral calculation.

The last column in Table I represents our final Tc $^-$ $J=0$ calculation, which contains the above second-order effects as well as select $4d^25s^2$ quadruple excitations. While these excitations also involve the $5s^2$ subgroup, with no analogous configurations needed in the neutral calculation, care must be taken not to unduly correlate the problem $4d^6vp^2$ configuration with $4d^2$ pair excitations that were deliberately left out of the DF manifold’s correlation (see Sec. II). We, therefore, include only those quadruple excitations that represent application of the four largest excitations to themselves and each other: $4d^25s^2 \rightarrow s^2d^2 + sp^2d + p^4 + p^3f + p^2f^2$. We note that, in particular, the last quadruple excitation is effectively $4d^2 \rightarrow f^2$ (always a large contributor to a level’s energy) added to $4d^6vp^2$. However, we have avoided overly preferential treatment of the problem configuration by leaving out other important $4d^2$ excitations, such as $4d^2 \rightarrow d^2$ (in the form of $4d^25s^2 \rightarrow p^2d^2$). Additionally, the fact that the $4d^6vp^2$ configuration has not regained the complete 130+ meV lost be-

tween its two configuration calculation contribution of ~ 500 meV to the complete first-order RCI contribution of 367 meV suggests that its manifold has not been artificially lowered below its position in smaller valence calculations.

The grouped excitations in Table I go up to $\ell=4$ (vg), except for $4d5s \rightarrow \ell\ell'$, which also includes $4d5s \rightarrow fh$, which gives a net differential contribution of ~ 10 meV in favor of the negative-ion states. The $4p^2$ double excitations are included because they contain the exclusion type excitations into the open $5s$ subshell present only in the neutral threshold, while the $4p-5s$ pairs are likewise exclusion type excitations out of the differently occupied $5s$ subshell. Corresponding $4p-4d$ pairs are omitted as they are expected to be nearly equal in the neutral and negative ions just as the $4d^2$ pairs were shown to be. Single excitations out of the $4p$ subshell are found to differ by only ~ 10 meV (with $4p \rightarrow f$ giving a correlation contribution of ~ 1.8 eV in both states) and are also excluded to reduce the pulling away problem discussed above and in Sec. II.

Finally, BE’s are calculated using the previously mentioned intermediate stage $4d^65s^2$ level separations. The resulting BE’s for $J=4,3,2,1,0$ levels are 636, 552, 503, 481, and 460 meV, respectively. In Fig. 1 we present the plot of s -electron binding energies [17] for the second transition series along with our RCI Tc $^-$ $J=4$ EA and the least-squares fit to the $n=7$ through $n=10$ data. Points for $n=1$ and $n=2$ are not present in such a plot as the measured negative-ion states of Sr and Y are p attachments [1,17,18] to the $4d^{n-1}5s^2$ neutral ground states. We note that within our general expected accuracy of 30 meV in EA calculations [11,12], our result of 636 meV supports our own semiempirical estimate of 658 meV, suggesting that d^6s^2 s -electron BE’s in transition metal series follow the linear trend (see Fig. 1) of the corresponding $d^n s^2$ $7 \leq n \leq 10$ states.

RCI calculations were also done for Re $^-$ $5d^66s^2$ $J=4$. Their quality was similar to those for Tc $^-$, and the result suggests Re $^-$ is slightly (< 10 meV) unbound. Also, a

crude, but sufficient, RCI calculation on Mn^- confirms the semiempirical prediction that it is unbound by more than 1.0 eV.

The discrepancy with our revised predicted EA of 61 meV, given our good agreement in the Tc^- case, can be understood by comparing total RCI contributions between the two systems. As mentioned in Sec. I, the difference in energy between the d^6s threshold and the ground state is much greater for Re I than Tc I, 1.46 eV vs 0.32 eV [4]. Even given the difference in RCI EA's of ~ 0.64 eV, we see that the total correlation energy is approximately 0.5 eV greater in Re^- (the two systems are unbound with respect to the excited threshold by nearly the same amount at the DF level, so the difference in total correlation is approximately equal to the difference in binding energy with respect to the excited thresholds). In general, the larger the correlation, the larger the "pulling away" of correlation configurations and second-order losses. The Re^- calculation is further complicated by

the fact that the $J=4$ level is the only one likely to be bound, so we cannot use our relative positioning method as we did in working with the much simpler $\text{Tc}^- J=0$ calculation. The result is that small losses appear due to the need of reducing basis size and necessarily less thorough attempts at virtual basis set saturation both in the first-order contributions and second-order corrections. Even if this calculation were improved, for example, by further opening of the core, we are unlikely at this stage to see Re^- bound by more than 20–30 meV in our RCI calculation. Since we prefer an error estimate of ~ 30 meV for EA, our calculations are unable to ascertain whether or not Re^- is bound. Semiempirical results [1,2] manifest a similar uncertainty.

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